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13. ABSTRACT *(Maximum 200 words)*

The overall objective was to develop methods to determine the factors that control how low-level mixtures of PAHs degrade aerobically in marine sediment systems, in order to determine what rate and extent of biodegradation can be expected in marine sediments under natural and engineered conditions. Specifically, this expansion was added to provide the capability to examine the effects of sediment grain size on laboratory and field observations of PAH behavior. Studies were carried out to characterize the performance of a prototype, bench-top Laser in Situ Scattering Transmissometer (LISST) under a variety of conditions to determine its utility and limitations in the laboratory and field. The impact of grain size effects on experimental and field interpretation was examined. Since grain size is one of the controlling parameters for contaminant distribution, an understanding of the behavior and fate of particles in the field and laboratory as a function of grain size reveals much about the behavior and fate of contaminants in the same environments. These studies have allowed us to optimize these tools to address those goals, and to put the strengths and limitations of the methods in perspective.

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GRANT TITLE: Fate of Complex Aromatic Petroleum Hydrocarbons in Marine Sediments: Biological Transformation, Degradation, and Sequestration - Supplement

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OBJECTIVE: The overall objective was to develop methods to determine the factors that control how low-level mixtures of PAHs degrade aerobically in marine sediment systems, in order to determine what rate and extent of biodegradation can be expected in marine sediments under natural and engineered conditions. Specifically, this expansion was added to provide the capability to examine the effects of sediment grain size on laboratory and field observations of PAH behavior.

APPROACH: Studies were carried out to characterize the performance of a prototype, bench-top Laser in Situ Scattering Transmissometer (LISST) under a variety of conditions to determine its utility and limitations in the laboratory and field. The impact of grain size effects on experimental and field interpretation was examined.

ACCOMPLISHMENTS: 1) Demonstrated the effects of sampling biases on grain size (and thus PAH) distribution in slurry experiments; developed methods for minimizing these effects using control sediments. 2) Designed new methods for removing representative samples from slurry systems with a minimum of grain-size bias. 3) Carried out extensive studies to characterize the performance of a prototype, bench-top Laser in Situ Scattering Transmissometer (LISST) under a variety of conditions to determine its utility and limitations in the laboratory and field. LISST is based upon fundamentally different processes to determine grain size than are standard sieving or settling methods. LISST measures the scattering angle spectrum of a particle suspension, and then deconvolutes the signal to determine the particle volume at various grain sizes. Thus, it is non-destructive. However, it is important to compare the performance of this method to standard methods, if data are to be compared and integrated. The effects of methodological parameters such as flow and stirring rate, sample dilution and suspension ionic strength were evaluated, and a standard method was developed. During

this time, the instrument, which was a prototype unit, was returned to the manufacturer for repair and/or refinement a few times. Once methods had been refined, LISST grain size results for sediments were compared to results based upon standard methods - sieving and stokes settling. While roughly comparable, there were significant differences between these methods, and these were documented in detail. Then, LISST performance with single and mixed grain-sized standards was evaluated, and size-specific correction factors were investigated. Finally, the performance of the bench-top LISST unit was compared to that of an in-situ unit. The results of all these studies, and their implications for the use in laboratory and field studies, are the subject of a manuscript in preparation.

CONCLUSIONS: LISST is being used in ever more studies as a laboratory, in situ or on-site tool for tracking particle behavior in sediment systems. However, little work has been done to address the effects of measurement parameters or field conditions on LISST results and interpretation. While it should be pointed out that no method to measure parameters in natural systems represents the "truth" and that all methods involve assumptions and biases, particular caution should be applied when a commonly measured parameter is measured in a fundamentally different way. Investigation of LISST performance in a number of laboratory and field conditions provided the opportunity to optimize measurement methods, and to provide extensive information about the similarities and differences between LISST and standard methods. LISST allows scientists to track behavior of sediments as a function of grain size under a variety of conditions that are impossible by standard methods - measurements can be in situ with no change of salinity, and with vanishingly small samples. The results of all these studies, and their implications for the use in laboratory and field studies, are the subject of a manuscript in preparation. Since grain size is one of the controlling parameters for contaminant distribution, an understanding of the behavior and fate of particles in the field and laboratory as a function of grain size reveals much about the behavior and fate of contaminants in the same environments. These studies have allowed us to optimize these tools to address those goals, and to put the strengths and limitations of the methods in perspective.

SIGNIFICANCE: An important parameter in explaining contaminant behavior in marine sediments and in suspended

particles in seawater is the grain size distribution of the particles. This, along with specific surface area and percent organic carbon, goes a long way in helping predict PAH and other contaminant partitioning, availability and potential biodegradability. It has often been predicted that differences in PAH concentrations in suspended sediments and in-place sediments is a grain size effect - suspended sediments are more concentrated in fine-grained material, and thus relatively enriched in sorbed PAHs. Alternatively, differences in PAH levels are interpreted as evidence of in situ biodegradation. It is important to deconvolute these two effects to aid in modeling of in situ biodegradation rates. In the laboratory, sampling slurries during biodegradation experiments can selectively remove the fine-grained, PAH-rich particles (which are suspended in the slurry) relative to the coarse-grained, PAH-poor particles (which are on the flask bottom), causing aritifacts that can be misinterpreted as evidence of biodegradation. Modeling PAH behavior in sediment systems requires knowledge of the sediment characteristics, including grain size distribution. All of the above make clear that sediment grain size distribution, as a function of sample type, time, or experimental procedure, can affect the way we model and interpret PAH behavior in field and laboratory systems. However, in many cases, samples are too small for grain size to be analyzed by the standard sieving or settling, dewatering and weighing process. Laser in situ scattering transmissometry (LISST) allows for the analysis of trends in grain size distribution of small samples - either directly in solution from the field (suspended solids) or during sample analyses. This non-destructive method will provide insight that is critical to experimental interpretation, and field modeling efforts. An added value is that field portable LISST can provide on-site information during a sampling effort, which, when combined with other field screening tools, helps guide sampling to assure that sediments collected in the field are appropriate for experimental requirements. Like all analytical methods, the methods by which LISST tools determine grain size distribution have some limitations and biases. This work has demonstrated some of the limitations of the use of LISST in a field or laboratory effort, which should lead to better use of data, and new insights into contaminant behavior in laboratory and field systems.

PATENT INFORMATION: None.

AWARD INFORMATION: Promoted to DP-IV (GS 14/15)

PUBLICATIONS AND ABSTRACTS (for total period of grant):

1. E Arias and S Apitz (in prep) "The use of laser in situ scattering transmissometry (LISST) for grain size distribution in the field - an evaluation of strengths and limitations"

2. S Apitz and E Arias (in prep) "Sampling biases in slurry experiments - implications and solutions"